Nodulised stack dust (NSD) as a lime and potassium source for grapes

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Abstract

This three year project, aimed to test the efficacy of nodulised stack dust (NSD), as a cost effective alternative to lime and potassium sulphate (SOP) on grapes. As NSD contains traces of thallium (Tl), intensive monitoring of soil, plant and fermented juice (must) was necessary to ensure the product was safe for the wine industry, and whether any guidelines were needed for its use. This study was undertaken in Brightwater, Nelson using two grape varieties, Pinot Noir and Sauvignon Blanc. There were seven replicated treatments; a nil control, along with two rates of NSD, their two equivalents as a lime + SOP blend and two rates of SOP alone. In both varieties, and in all years, the higher rate of NSD and lime + SOP significantly increased soil pH over the control, and for NSD over the SOP alone treatments. NSD was slightly more effective in raising soil pH than lime + SOP. In contrast, in both varieties, SOP alone was more effective at initially increasing soil potassium (K) levels. By year 3, differences between NSD and lime + SOP were not significant. The higher K rate was more effective in increasing soil K levels. Potassium levels were not significantly different in leaf petioles between the main treatments. However in year 3, in both varieties, the higher K rates resulted in significantly higher K levels than the lower rate. From year 2, in both varieties, all K treatments gave darker foliage than the control. Yield estimates showed a similar trend. In year 3, bunch weights for the control treatment were significantly lower than in all K treatments, (16% lower in Pinot Noir, 20% lower in Sauvignon Blanc). Only small differences were noted in juice quality before and after primary fermentation. However, liming treatments often gave small increases in pH and lower titratable acidities (TA), than SOP alone. NSD increased the soil Tl levels as the trial progressed, particularly when used at the higher rate. However soil Tl levels remained low, and it would take many years of continuous use, for this to reach the suggested maximum permissible levels for New Zealand soils. There was limited uptake of Tl by leaf petioles, and present in fermented juice, with results often barely above analytical detection levels. This work shows that NSD is a suitable alternative to lime and SOP for grapes. Thallium would not be an issue in the short to medium term and should be monitored every 3-5 years. Grapes on these soils would benefit from 40-80 kg K/ha/annum with no detriment to juice quality.

Additional keywords: potassium sulphate, cement kiln dust, must pH, thallium

Introduction

Nodulised stack dust (NSD) or kiln dust is a by-product of the cement industry. Fine precipitator dust (<10 µm in size) is generated in the cement kilns when limestone and marl are heated to make clinker, the first stage in making cement. The Holcim plant at Westport, and the Golden Bay Cement plant at Whangarei, sell kiln dust as a fertiliser source. As kiln dust is difficult to transport and spread, the Buller Community Fertiliser Company (BCFC) at Westport, granulate the dust to form NSD. Kiln dust acts as both a liming source and a source of potassium (K). It has been used for over 30 years by dairy farmers in Buller, the West Coast, and Golden Bay. Previous studies, by MAF in the late 1980's, showed NSD to be an effective source of lime and K on pasture (Jeff Morton pers. comm., 1988). Kiln dust is known to contain some trace elements, which are concentrated in the cement kilns, thallium (Tl), in particular being of concern.

In the late 1990's, routine sampling by Ravensdown Fertiliser Co-op, BCFC and others suggested that Tl levels in NSD, sometimes exceeded 100 ppm, although results varied due to differing laboratory analytical techniques. To investigate this, Holcim, BCFC, and Ravensdown, commissioned AgResearch Limited to undertake a survey of dairy farms. From this, recommendations for the use of NSD on pasture were made (Roberts and Longhurst, 2001), to control soil accumulation of Tl and minimise it's impact on livestock and the environment. As a follow up, BCFC commissioned Nutrient Solutions Ltd to monitor Tl levels on several dairy farms with variable histories of NSD use. This work has established protocols and guidelines, which have reduced Tl accumulation in the soil, and reduced herbage uptake. Together, with collaboration from BCFC and Holcim, Tl levels in NSD have also dropped, averaging <25 ppm, for the past three years (Craighead, 2011b.).

In recent years, NSD has been used by the grape industry, firstly because it contains K in the low salt index sulphate form, as required by grapes (Leymonie, 1990), and secondly because it is a cost effective source of lime and K in Marlborough and Nelson. While K is required for vine health and yield, there is concern by winemakers that use of K can be detrimental to juice quality by excessively increasing the must pH (Etourneaud, 1996). As NSD's efficacy as a K source for grapes was unknown, and in an effort to clarify some juice quality issues, a three year trial was undertaken on grapes comparing NSD with conventional lime and K fertiliser. This included monitoring Tl levels in control and NSD treatments.

Material and Methods

The property chosen for this work was owned by the Lindsay family, Brightwater, Nelson (41° 22' 26" S, 173° 07' 41" E), where NSD had previously been used. The specific site had not received any NSD inputs since November 2004, well before the commencement of this trial. Both nine to ten year old Pinot Noir and Sauvignon Blanc grapes were used to reflect differences in wine quality; red grapes have the potential to show greater differences than white grapes as their skins are in contact with the juice during primary fermentation. Both varieties were grown at the same site, 20-30 m apart. The trials ran from 2008-9 (year 1) to the 2010-11 season (year 3). Prior to grape vines, the site was in dairy pasture.

The soil at the trial location is a Richmond Gley soil over gravels on the Waimea Plains, Nelson. Soil pH's were 6.4 (Pinot Noir) and 6.6 (Sauvignon Blanc). The cation exchange capacity of the sites was moderate, 18 and 19 me/100g respectively, however the sites were naturally high in magnesium (Mg), 4.1 and 4.4 me/100g (Kay and Hill, 1998), typical of this side of the Waimea Plain. Potassium (K) reserves were medium, 0.29 and 0.30 me/100g respectively (Cornforth and Sinclair, 1984), and likely to be responsive to K (Etourneaud, 1996). Previous monitoring of the Sauvignon Blanc block confirmed this. Annual rainfall was 1000-1100 mm/year supplemented when necessary by trickle irrigation.

Seven treatments were used, a control, and two rates of K as NSD, lime + SOP (sulphate of potash or potassium sulphate), or SOP, as outlined below.

(1) Control (base fertiliser only).
(2) NSD at 740-850 kg/ha (depending on the K concentration).
(3) NSD at 1480-1690 kg/ha.
(4) Lime at 440-590 kg/ha + SOP (K_2SO_4), 95 kg/ha.
(5) Lime at 880-1180 kg/ha + SOP (K_2SO_4) at 190 kg/ha.
(6) SOP (K_2SO_4) at 95 kg/ha.
(7) SOP (K_2SO_4) at 190 kg/ha.

The K in NSD is primarily in the sulphate form with its liming effect being mainly associated with alkalis such as calcium oxides, calcium carbonates and some hydroxides (Kingett Mitchell and Associates Ltd pers. comm., 1993).

The lower rate of NSD was chosen to provide 40 kg K/ha, typical of that required by the crop, and as previously used by the grower. Fertiliser was banded within a metre of the vines, as trafficking and trickle irrigation confined surface feeder roots close to the vine. The higher K rate used was designed to ensure an excessive loading of Tl, when K was applied in NSD. Samples of fresh NSD from different stock piles within the BCFC store were analysed for K and Tl, and blended to produce a NSD that reflected the average concentrations found in NSD during that season. In year 1, the NSD used contained 58 mg/kg Tl, and in year 2, 51 mg/kg Tl, the long term averages since monitoring of Tl commenced in 2001. However in year 3, the NSD contained only 20 mg/kg Tl, the level typical of the product produced in the previous two years, 2010-2011. To increase the actual soil Tl loading only slightly in year 3, a lower K concentration product was deliberately used. The NSD used contained 5.4% K and SO_4-S 3.5% (year 1); 5.8% K and 3.8% SO_4-S (year 2); and 4.7% K and 3.6% SO_4-S in year 3.

Lime rates were chosen to meet the same neutralizing value, (i.e. rates that caused the same change in pH), as NSD; in year 1, NSD 64%, lime 91%; in year 2, NSD 57%, lime 92%; in year 3 NSD 62%, lime 89%. Lime came from the same quarry as the marl used in cement manufacture.

Each treatment was replicated four times, a replicate consisted of one row (containing 25 bays). Within each row, treatments were randomised, and each plot consisted of three bays. Sauvignon Blanc grapes were on wide plant spacings of 1.5 m, equating to four plants in each bay (12 vines/plot). Pinot Noir grapes were on 1.2 m plant spacings, equating to five plants in each bay (15 plants/plot). Rows were 3 m apart, and for each variety four adjacent rows were used.

All plots received basal phosphate (P), sulphur (S) and nitrogen (N); in year 1, 13 kg P, 16 kg S and 26 kg N /ha, reducing to 9 kg P, 11 kg S and 7 kg N in years 2 and 3, to mimic the grower's use. In year 1, these were not applied until November 2008, as approval for the project was not received until late October. Rain, within a week of application, hastened dissolution of fertiliser products. In years 2 and 3, treatments were applied in late August, in advance of budburst. Vines received appropriate plant protection and cultural management in line with the rest of the vineyard. In years 2 and 3, fish oil, 10-20 l/ha, was also applied (containing 0.18% K).

Vines were initially winter pruned to four canes, however in years 2 and 3, the Sauvignon Blanc was pruned to three canes, as yields were excessive. In winter, both blocks were grazed with sheep. In year 2, the balance of the Sauvignon Blanc block was ripped out as the grower lost his largest contract. As the sheep farmer winter grazing the block initially failed to fence off the trial area after budburst, ewes severely damaged the first leaves and fruit buds. While it was possible to later measure herbage K concentration and colour, no yield or juice quality data was possible in year 2.

Measurements and assessments were as follows.

Soil

pH, K, and Tl were analysed by ARL Laboratories, Napier, for pH (Blakemore *et al*., 1987) and exchangeable K (Rayment and Higginson, 1992), and for Tl (using a nitric acid/hydrochloric acid digestion and ICP-MS analysis). Samples were to 15 cm, taken annually at the end of the season, (June-July), within the drip zone, 15 cores/plot.

Herbage

Petioles were sampled in early summer from the leaf opposite the bunch (Kay and Hill, 1998), and analysed for K by ARL Laboratories, (nitric acid/hydrogen peroxide digestion, ICP-MS analysis), and Tl by Hill Laboratories, Hamilton, using a biological materials digestion and ICP-MS analysis. Sampling was delayed until early February (year 1) due to the late application of fertiliser treatments, and in year 2 on the Sauvignon Blanc site until sufficient regrowth was available to sample. In year 3 sampling was brought forward until late November, rather than December, in an attempt to better differentiate among treatments.

Colour scoring

Foliage was also scored in early December, using a 0-10 scale for colour developed for this purpose, where 0 represented yellow foliage, and 10, dark green foliage. Both aspects of the canopy were scored due to variation in light interception, but only mean results are presented.

Yield

It was impossible to hand harvest all plots within the restricted timeframe associated with the commercial vineyard operation, and without causing any potential quality variability across the trial through a protracted harvest window. In year 1, the centre bay of each plot was hand harvested, however as these only represented four or five plants the variability was too great to reflect treatment effects, so results are not presented. To overcome this, yields for the whole bay were estimated (both sides of the row assessed on a 0-10 scale, 0 = low, 10 = high), prior to a fixed number of bunches being representatively harvested from each plot, for juice assessment. In addition, bunch size was scored in years 2 (Pinot Noir) and 3 (both varieties), before being measured in year 3 (60+ bunches for Pinot Noir and 48+ bunches for Sauvignon Blanc). These numbers gave sufficient volume for juice quality measurements.

Grapes were harvested in the second week of April 2009, (end of year 1), the first week of April 2010, (year 2), and the last week of March 2011, (year 3). In year 1 when there was more pressure to harvest early, grapes were less mature than years 2 and 3. Samples of 5.5-7.5 kg were taken for quality purposes and transported to Amberley, North Canterbury where mini-ferments took place as follows.

Pinot Noir

Samples of 5 kg (year 1), and 6 kg (years 2 and 3), were crushed by hand in a bucket, and left to settle for 24 hours in cool conditions. Brix sugar (measured by refractometer), pH and titratable acidity (TA) were measured on a sub-sample. A yeast solution (*Saccharomyces cerevisiae*, 0.2 g/l), was added to each bucket and the juice kept at a temperature with as minimal day/night variation as possible. Grapes were plunged twice a day during fermentation, (12-14 days). Alcohol/sugar content was monitored by hydrometer until primary fermentation was complete. Juice was then extracted (55% extraction) using a hand press. A sub-sample was taken for post ferment pH and TA, with another sample sent where applicable, to Hill Laboratories for Tl measurement.

Sauvignon Blanc

In years 1 and 3, a 6 kg sample was crushed at Sherwood Estate winery, Waipara, (50% extraction), and allowed to settle for 24 hours in cool conditions. Sub-samples were taken for brix, pH and TA as for the Pinot Noir. A similar yeast solution was added to each bucket under the same conditions used for the Pinot Noir. In year 1, food grade DAP (diammonium phosphate), 400 ppm, was also added, split equally between day 1 and day 8. Alcohol/sugar content was monitored by hydrometer until primary fermentation was complete and sub-samples kept for pH, TA, and where applicable Tl analysis.

Additional heavy metal data, comparing the initial background levels for each site, with the bulked treatment samples within each site at the end of the trial, are given in Craighead (2011a).

Statistical analysis of variance and correlation were carried out using Minitab (Minitab, Inc., Pennsylvania, USA). For analysis of variance (ANOVA), treatment effects were expressed as least significant difference (LSD) ($P=0.05$).

Results and Discussion

Soil pH

From year 1, with both varieties, the higher rate of NSD, significantly lifted soil pH over that of the control and SOP-only treatments, with differences becoming greater with time (Table 1). The higher rate of lime + SOP significantly lifted soil pH over the control in both varieties, and in Sauvignon Blanc over the SOP-only treatments, from year 1. The lower rate of NSD or lime + SOP significantly lifted the pH above the control by year 3, especially on the Sauvignon Blanc site. There were no significant differences between SOP alone and the control, at any time.

There was little difference between the NSD and lime + SOP treatments. High rates of NSD were marginally better than lime +

SOP in increasing pH, in both varieties. NSD contains finer particles than lime and more alkaline oxides and hydroxides, as opposed to the carbonates present in lime. In later years, differences should be minimised as the coarser fractions of agricultural lime initially applied, start dissolving (Craighead, 2005). NSD has previously initially increased soil pH under pasture, when compared to lime (Jeff Morton pers. comm., 1988).

Soil pH from NSD and lime + SOP were high by the end of the trial (Kay and Hill, 1998), especially on the Sauvignon Blanc site, so would not need liming for several years.

Table 1: Soil pH and exchangeable K values (0-15 cm depth), in Pinot Noir and Sauvignon Blanc grapes, at the end of each season, year 1 (2008-9), year 2 (2009-10) and year 3 (2010-11) for seven treatments.

Treatment	Pinot Noir						Sauvignon Blanc					
	Year 1		Year 2		Year 3		Year 1		Year 2		Year 3	
	pH	K me/100g	pH	K me/100g	pH	K me/100g	pH	K me/100g	pH	K me/100g	pH	K me/100g
Control	6.600	0.360	6.550	0.360	6.575	0.278	6.700	0.303	6.700	0.325	6.700	0.263
NSD low	6.675	0.340	6.675	0.383	6.750	0.308	6.775	0.320	6.775	0.318	6.975	0.280
NSD high	6.775	0.363	6.750	0.385	6.850	0.330	6.950	0.325	6.875	0.373	7.050	0.330
Lime + SOP low	6.675	0.378	6.650	0.378	6.750	0.330	6.750	0.355	6.775	0.335	6.925	0.325
Lime + SOP high	6.750	0.430	6.700	0.410	6.825	0.365	6.925	0.358	6.925	0.345	7.025	0.333
SOP low	6.575	0.408	6.600	0.398	6.550	0.343	6.650	0.370	6.625	0.328	6.650	0.323
SOP high	6.650	0.418	6.575	0.405	6.625	0.375	6.725	0.375	6.750	0.360	6.750	0.343
$LSD_{(0.05)}$	0.119	0.073	0.121	ns[1]	0.098	0.075	0.136	0.052	0.130	0.046	0.128	0.055
Main effects - NSD versus lime + SOP												
Source of K	ns	*[2]	ns	ns	ns	ns	ns	**[3]	ns	ns	ns	ns
Rate of K	*	ns	ns	ns	**	ns	**	ns	**	*	**	ns
Source x K Rate	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

[1]ns = not significant, [2]* = LSD>0.05<0.1, [3]** = LSD<0.05.

Soil Potassium

In year 1 for both varieties, SOP, particularly in the absence of lime, significantly lifted soil K over a low rate of NSD, and in Sauvignon Blanc over the control. SOP alone is likely to be more a more effective K source, due to less competition from the calcium (Ca) in the liming treatments, for soil cation exchange sites. Potassium treatment differences were less pronounced in years 2 and 3, especially in Pinot Noir.

Higher rates of K tended to be more effective in lifting soil K than low rates, although differences were not always significant. In the case of NSD this possibly reflects a delay in release of K from some of the larger NSD nodules (some were present on the soil surface up to a year after application). It is also possible some of the fine K fractions in NSD have quickly dissolved, leading to enhanced plant uptake from NSD, as discussed elsewhere in the paper, at the expense of soil accumulation. Small, but not significant differences in soil K were still evident at the end of three years, between NSD and lime + SOP. Previous work on cement kiln flue dust using a range of soils in Canada has shown kiln dust to be as effective as SOP and gypsum in lifting soil K concentrations, as well as yields and leaf tissue concentrations, in potato, barley and lucerne (van Lierop *et al*., 1982).

Potassium levels were lower on both sites in year 3 (2010-11), possibly as a consequence of higher leaching and higher yields, due to a wetter, but sunnier season than the previous two years.

Herbage Leaf Colour

In both varieties, all K treatments darkened the greenness of the mature foliage from year 2 (Table 2), with some treatments also greener than the control in the first year. In the second year, higher rates of K gave significantly darker foliage, in both varieties, especially SOP treatments. Potassium sulphate is known to darken foliage, as it favours chlorophyll and carotene content which in turn leads to improved growth (Leymonie, 1990).

NSD was generally more effective at darkening the foliage than lime + SOP, irrespective of rate and variety. The presence of lime with SOP had little effect on the colour of Pinot Noir leaves, but in Sauvignon Blanc, leaves often had a better colour in the absence of lime. Differences on the Sauvignon Blanc site might be understandable, given that the soil pH and Ca levels were higher than on the Pinot Noir site. Therefore there was more cation competition for soil exchange sites in the presence of lime, and hence a greater risk of winter leaching of K, and less likelihood of plant uptake. However the effect is less clear when comparing NSD with lime + SOP, unless the fines in NSD are contributing to more plant available K.

Table 2: Leaf colour (0-10 score, 0 = pale yellow, 10 = dark green), and leaf petiole K%, for Pinot Noir and Sauvignon Blanc grapes during each season, year 1 (2008-9), year 2 (2009-10) and year 3 (2010-11), for seven treatments.

Treatment	Pinot Noir						Sauvignon Blanc					
	Year 1		Year 2		Year 3		Year 1		Year 2		Year 3	
	Colour 0-10 score	Petiole K %	Colour 0-10 score	Petiole K %	Colour 0-10 score	Petiole K %	Colour 0-10 score	Petiole K %	Colour 0-10 score	Petiole K %	Colour 0-10 score	Petiole K %
Control	6.13	1.03	5.00	1.28	4.44	1.68	6.00	1.30	5.13	3.88	4.31	1.83
NSD low	6.13	0.95	6.06	1.23	6.19	1.55	6.63	1.38	5.75	3.78	5.06	1.75
NSD high	7.00	1.00	6.31	1.35	6.00	1.75	6.63	1.48	6.06	3.65	5.63	1.98
Lime + SOP low	6.13	1.05	5.75	1.28	5.50	1.48	6.38	1.40	5.75	3.80	4.94	1.63
Lime + SOP high	6.25	1.03	6.19	1.15	5.56	1.68	5.88	1.25	6.50	4.00	4.94	1.78
SOP low	6.25	1.10	5.75	1.25	5.75	1.65	6.25	1.35	6.00	3.75	4.94	1.68
SOP high	6.25	0.95	5.94	1.25	5.56	1.68	6.75	1.23	6.69	3.53	5.56	1.93
LSD$_{(0.05)}$	0.52	ns[1]	0.37	ns	0.62	ns	0.58	ns	0.40	ns	0.56	0.15
Main effects - NSD versus lime + SOP												
Source of K	ns	ns	*[2]	ns	**[3]	ns	**	ns	*	ns	**	**
Rate of K	*	ns	**	ns	ns	*	ns	ns	**	ns	ns	**
Source x K Rate	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

[1]ns = not significant, [2]* = LSD>0.05<0.1, [3]** = LSD<0.05.

Herbage Petiole Potassium

Despite K treatments darkening the foliage there were no treatment effects on bunch leaf petiole K levels, in any year, with either variety. However in year 3, when sampling was earlier, there was a rate of K response in both varieties, especially Sauvignon Blanc. Further, when comparing NSD with lime + SOP, K levels were also higher with NSD at both rates, suggesting improved K uptake. Comparisons of SOP with and without lime, gave variable K responses on both varieties.

Foliage K levels will also be influenced by the leaf size and the total amount of foliage grown. In healthy plants herbage levels decline with leaf expansion, (Smart *et al*., 1986). While leaf size and canopy volume were not specifically measured, in year 3 it was noticeable that the control leaves were smaller and foliage thinner, compared with all other treatments. As the canopy was reasonably similar amongst the six K treatments, the rate response trends observed in year 3, must be related to plant uptake of K, rather than canopy dilution.

Petiole K levels were high in Sauvignon Blanc in year 2, as there was no fruit present. With anticipated yields equivalent to 15 t/ha, then 40-50 kg K/ha might be expected to be removed by fruit, and in this instance this was retained in the foliage (Etourneaud, 1996; SCPA, 1994; Smart *et al*., 1986).

Only in year 3, was there limited correlation between winter soil K tests and subsequent petiole K levels, (r=0.43 in Pinot Noir and 0.33 in Sauvignon Blanc). Work by Etourneaud (1996) showed similar poor correlations between soil and leaf K but the ratio of K to cation exchange capacity (CEC), i.e. % base saturation (BS), showed good relationships with plant K (r=0.63-0.72) using soils with various clay contents. Etourneaud (1996) suggested K should lie between 1.5 and 3% of the CEC; in this work the sites commenced at 1.6% rising with K fertilisers to over 2% by the end of the trials, suggesting the sites would be slightly K responsive. In New Zealand agricultural and horticultural soils, it is generally accepted that % BS should lie between 2-6% for K and 5-15% for Mg, (Kay and Hill, 1998); on these sites as Mg is >20% BS then Mg is likely to be inducing K responses and causing poor relationships between the measured K parameters.

Harvest Yield Parameters

In both varieties, the control always had the lowest yield estimate and bunch size, Table 3. The control estimated yield was significantly lower than all other treatments in year 2 (Pinot Noir), and year 3 (Sauvignon Blanc). There were no differences between NSD and lime + SOP with either assessment. The addition of lime to SOP gave variable responses. Bunch size estimates showed little treatment variation in the Sauvignon Blanc; this may have been as it was pruned to three canes, thereby causing less yield dilution than if it had carried four canes, and hence more bunches. The trends observed when scoring bunch size were confirmed in year 3 when bunch weight was measured. In both varieties, the control had significantly lower bunch weight than all K treatments, (16% Pinot Noir, 20% Sauvignon Blanc). However, there were no differences between K treatments or rate of K application. Bunch weight (berry size), has previously been shown to be an indicator of K deficiency (Weir and Cresswell, 1993).

Table 3: Plot yield estimates (0-10 score, 0 = low, 10 = high), year 1 (2008-9), year 2 (2009-10) and year 3 (2010-11) for Pinot Noir, years 1 and 3 (Sauvignon Blanc); bunch size estimates (0-10 score, 0= small, 10 = large), in years 2 (Pinot Noir) and 3 (Pinot Noir and Sauvignon Blanc); bunch weight (year 3), on both varieties, for seven treatments.

Treatment	Pinot Noir						Sauvignon Blanc			
	Year 1	Year 2		Year 3			Year 1	Year 3		
	Estimated Yield	Estimated Yield	Estimated Bunch Size	Estimated Yield	Estimated Bunch Size	Bunch Weight	Estimated Yield	Estimated Yield	Estimated Bunch Size	Bunch Weight
	0-10 score	0-10 score		0-10 score		g	0-10 score	0-10 score		g
Control	5.38	5.54	4.75	5.25	4.88	114.3	5.75	5.00	5.75	141.0
NSD low	5.88	6.70	6.13	6.19	6.25	128.0	6.38	6.00	6.38	175.3
NSD high	6.13	6.66	6.31	6.63	6.75	135.8	6.38	6.06	6.50	164.3
Lime + SOP low	6.00	6.38	6.25	6.44	6.25	131.3	5.88	6.13	6.50	164.8
Lime + SOP high	5.63	7.06	6.88	6.25	6.13	131.8	6.13	6.25	6.38	178.0
SOP low	5.88	6.55	6.75	6.19	6.38	138.5	6.13	5.69	6.25	164.8
SOP high	6.13	6.42	5.94	6.25	6.13	131.3	6.75	5.81	6.38	165.8
$LSD_{(0.05)}$	ns[1]	0.42	1.27	1.01	1.24	11.8	0.65	0.50	ns	14.2
Main effects - NSD versus lime + SOP										
Source of K	ns	ns	ns	ns	ns	ns	**[3]	ns	ns	ns
Rate of K	ns	*[2]	ns	ns	ns	ns	ns	ns	ns	ns
Source x K Rate	ns	ns	ns	ns	ns	ns	ns	ns	ns	**

[1]ns = not significant, [2]* = LSD>0.05<0.1, [3]** = LSD<0.05.

Juice Quality - Pinot Noir

Small differences in juice quality, (particularly pH), were observed in years 1 and 3 (Table 4). Brix levels at harvest improved each year. Levels were low in year 1, due to pressure to harvest early, while year 3 had more sunshine hours and low harvest pressure. Primary fermentation took 12-14 days which was typical. Juice pH's were fairly typical of red wines pre-ferment, and all increased after primary fermentation, due to the release of cations from the skins present (Rankine, 2006). Titratable acidity values were at the upper level of normal (4-8g/l), pre-ferment, particularly in years 1 and 3, and slightly dropped after primary fermentation in accordance with the final pH of these samples. The final levels would be considered typical of Pinot Noir prior to malolactic (secondary) fermentation.

In general, there were only small differences between NSD and lime + SOP. However, NSD treatments gave significantly higher pH post-ferment, in year 1, with a non-significant trend in the other years. This often led to lower TA's, particularly in year 3.

The rate of K tended to have more effect than the form of K applied. Lower rates of K generally lifted the pH and dropped the TA more than the high rate, particularly in year 3. The addition of lime to SOP caused little effect in any year.

Potentially an increased availability of K can improve the translocation of sugars from leaf to fruit, improving the harvest brix levels (SCPA, 1994). In these experiments this was not observed, possibly because as the site became more K responsive, the control matured more quickly and therefore had a higher brix level anyway. When K is used the K forms salts with acids. Salt formation can increase the juice pH and drop the TA, a factor of concern to oenologists as this could lead to reduced taste and keeping quality in wine (SCPA, 1994). Again, this was not observed, especially at the higher K rate, probably because the K was required to grow the canopy and improve the yield. In practical terms the differences in juice pH and TA caused by K fertiliser are small, and will be of limited importance to a winemaker.

Table 4: Pre-ferment juice sugar (by refractometry), pre- and post-ferment juice pH and TA for Pinot Noir grapes, year 1 (2008-9), year 2 (2009-10) and year 3 (2010-11), for seven treatments.

Year	Treatment	Pre-ferment Juice			Post-ferment Juice	
		Refractometry Sugar	pH	TA	pH	TA
2008-9 (year 1)	Control	21.03	3.43	7.88	3.54	7.88
	NSD low	21.43	3.44	7.75	3.57	7.83
	NSD high	19.93	3.41	8.16	3.53	8.07
	Lime + SOP low	20.93	3.42	7.92	3.51	8.03
	Lime + SOP high	20.73	3.41	7.62	3.49	7.94
	SOP low	20.18	3.41	8.14	3.48	8.07
	SOP high	20.90	3.40	8.07	3.49	8.01
	$LSD_{(0.05)}$	0.89	0.03	ns[1]	0.07	ns
	Main effects - NSD versus lime + SOP					
	Source of K	ns	ns	ns	**[3]	ns
	Rate of K	**	ns	ns	ns	ns
2009-10 (year 2)	Control	22.25	3.04	9.53	3.44	8.20
	NSD low	22.48	3.06	9.70	3.45	8.31
	NSD high	22.08	3.04	9.72	3.45	8.22
	Lime + SOP low	22.03	3.04	9.62	3.43	8.25
	Lime + SOP high	22.40	3.05	9.40	3.44	8.16
	SOP low	22.28	3.05	9.55	3.45	8.25
	SOP high	22.38	3.05	9.49	3.43	8.20
	$LSD_{(0.05)}$	ns	ns	ns	ns	ns
	Main effects - NSD versus lime + SOP					
	Source of K	ns	ns	ns	ns	ns
	Rate of K	ns	ns	ns	ns	ns
2010-11 (year 3)	Control	23.25	3.36	8.18	3.74	7.47
	NSD low	23.65	3.40	7.47	3.82	7.17
	NSD high	22.38	3.32	8.05	3.74	7.35
	Lime + SOP low	23.20	3.37	7.80	3.78	7.35
	Lime + SOP high	23.55	3.37	8.03	3.76	7.77
	SOP low	22.43	3.36	7.92	3.74	7.37
	SOP high	23.25	3.37	7.73	3.77	7.32
	$LSD_{(0.05)}$	1.20	0.05	0.38	ns	0.41
	Main effects - NSD versus lime + SOP					
	Source of K	ns	ns	ns	ns	**
	Rate of K	ns	*	**	ns	**

[1]ns = not significant, [2]* = LSD>0.05<0.1, [3]** = LSD<0.05.

Juice Quality - Sauvignon Blanc

There were only small treatment differences in sugar levels at harvest in both seasons, (Table 5). NSD had lower levels than lime + SOP in year 1. The reverse trend was noted in year 3. Higher rates of K had higher harvest brix sugar levels suggesting K improved sugar conversion (SCPA, 1994).

In both years, juice pH slightly declined after fermentation, and while these were slightly low, they are not atypical of New Zealand Sauvignon Blanc. In year 1, juice pH pre-ferment was significantly lower with SOP alone, at both rates of K, a trend which continued after fermentation. Juice pH differences were less pronounced in year 3, but after fermentation TA was again higher for the SOP alone treatments, particularly compared with lime + SOP. The higher rate of K has led to reduced TA, particularly post fermentation, (and higher pH), in accordance with the expected response to K (SCPA, 1994). In this situation, as the juice is overly acidic, the higher, (above maintenance) K input of 80 kg K/ha, would help to reduce juice acidity and make the wine less harsh to the palate.

There was a small response to the four lime treatments in terms of higher pH and reduced TA, despite the higher soil pH on this site, but differences between NSD and lime + SOP were small. The Ca (from the lime or NSD), together with the higher rate of K are probably more effective at reducing Mg uptake. Overall, like the Pinot Noir observations, K treatment differences for Sauvignon Blanc are small and of limited importance to winemakers.

Table 5: Pre-ferment juice sugar (by refractometry), pre- and post-ferment juice pH and TA for Sauvignon Blanc grapes, year 1 (2008-9), and year 3 (2010-11), for seven treatments.

Year	Treatment	Pre-ferment Juice			Post-ferment Juice	
		Refractometry Sugar	pH	TA	pH	TA
2008-9 (year 1)	Control	20.08	3.16	11.72	2.93	12.22
	NSD low	19.25	3.14	11.98	2.92	12.26
	NSD high	20.15	3.14	11.81	2.93	12.02
	Lime + SOP low	20.48	3.12	11.87	2.90	12.36
	Lime + SOP high	20.78	3.13	11.97	2.94	12.19
	SOP low	20.10	3.10	12.43	2.90	12.57
	SOP high	19.70	3.10	11.85	2.90	12.45
	$LSD_{(0.05)}$	1.19	0.03	ns[1]	ns	ns
	Main effects - NSD versus lime + SOP					
	Source of K	*[2]	ns	ns	ns	ns
	Rate of K	ns	ns	ns	ns	ns
	Form x K Rate	ns	ns	ns	ns	ns
2010-11 (year 3)	Control	20.68	2.97	11.46	2.91	12.38
	NSD low	20.95	2.98	11.61	2.92	12.55
	NSD high	21.15	2.96	11.08	2.94	12.19
	Lime + SOP low	20.30	2.97	11.04	2.93	12.34
	Lime + SOP high	21.08	2.96	11.31	2.95	12.04
	SOP low	20.53	2.96	11.72	2.92	12.81
	SOP high	20.98	2.99	11.22	2.93	12.38
	$LSD_{(0.05)}$	0.55	ns	0.63	0.03	0.61
	Main effects - NSD versus lime + SOP					
	Source of K	**[3]	ns	ns	ns	*
	Rate of K	**	ns	ns	ns	**
	Form x K Rate	**	ns	ns	ns	ns

[1]ns = not significant, [2]* = LSD>0.05<0.1, [3]** = LSD<0.05.

On both sites, the soils are low in K, requiring several years of above maintenance inputs of 40-60 kg K/ha to lift soil levels to ‘optimal’ levels (Kay and Hill, 1998) and give a better K:CEC balance (Etourneaud, 1996). Previous monitoring of this site has shown K enhances leaf retention, and this coupled with the observed yield responses in terms of bunch size (and darker foliage), provides a possible explanation of why K has generally had no detrimental effect on raising juice pH and excessively decreasing TA. The darker foliage is likely to be indicative of improved photosynthesis, which could lead to improved translocation of sugars, so K salts are unlikely to have excessively accumulated. A long term trial in Bordeaux found SOP enhanced production with only a small increase (0.15) in must pH, and that in blind tasting at K rates up to 100 kg K/ha, these rates gave the best wine quality in terms of aroma, taste and colour (SCPA, 1994). In New Zealand these higher rates are unlikely to be valid for soils with high K reserves. Such soils exist in Marlborough, Waipara, Central Otago and parts of Hawkes Bay. Here K inputs should be minimal, (0-40 kg K/ha), especially as soils are often stony with lower yield expectations. Regular soil and plant monitoring is necessary to predict K responsive soils.

Thallium

Soil Thallium

NSD when used at the higher rate has significantly lifted soil Tl levels on both sites, particularly the Sauvignon Blanc block, which had a higher background level (Table 6). The low rate of NSD significantly lifted soil Tl levels above the control on both varieties by year 3, however the levels are still low, in many cases at the limit of detection. The suggested maximum permissible level (MPL) for New Zealand pastoral soils is 0.75 mg/kg (Roberts and Longhurst, 2001). Even if 1500 kg/ha of NSD were applied annually and contained 50 ppm Tl, (the long term average for NSD since 2001), then assuming a soil Bulk Density of 0.9, it would take eight more years for the soil Tl loading to reach the suggested MPL. This is also assuming no Tl moves below this sampling zone or is taken up by the plant. As some of this occurs, albeit at small levels, and given that the Tl average in NSD for the past two years has been 20 mg/kg (at 5.7% K), it could take 20 years to reach the suggested MPL. Given also that NSD would not be used every year as soil pH will not always be limiting, then soil Tl accumulation does not appear an issue in the short to medium term.

Plant Thallium

In all years, and both varieties, NSD treatments caused no significant effect on the bunch leaf petiole Tl levels, irrespective of the rate of application. Thallium levels were very low (suggested MPL for herbage 0.75 mg/kg, Craighead, 2011b). The Sauvignon Blanc site had higher levels due to the previous use of NSD. Petiole Tl levels have tended to decline with time, probably as a consequence of moving sampling forward each year, and particularly on the Pinot Noir site. In pasture, herbage Tl levels cycle annually and normally peak in February (Craighead, 2011b).

Table 6: End of season soil (0-15 cm), herbage (petiole) and fermented juice Tl concentrations for Pinot Noir and Sauvignon Blanc grapes, for three treatments, year 1 (2008-9), year 2 (2009-10) and year 3 (2010-11). No juice available for Tl analysis, year 2, for Sauvignon Blanc.

Treatment	Pinot Noir			Sauvignon Blanc		
	Year 1	Year 2	Year 3	Year 1	Year 2	Year 3
End of year soil Tl (0-15 cm)		mg/kg			mg/kg	
Control	0.190	0.190	0.195	0.198	0.190	0.207
NSD low	0.195	0.223	0.254	0.220	0.220	0.275
NSD high	0.213	0.250	0.266	0.255	0.275	0.306
$LSD_{(0.05)}$	0.017	ns[1]	0.042	0.041	0.069	0.054
Bunch Leaf Petiole Tl		mg/kg			mg/kg	
Control	0.034	0.015	0.014	0.081	0.043	0.044
NSD low	0.034	0.015	0.013	0.086	0.051	0.047
NSD high	0.035	0.016	0.015	0.084	0.044	0.049
$LSD_{(0.05)}$	ns	ns	ns	ns	ns	ns
Post-ferment juice Tl		mg/l			mg/l	
Control	0.00056	0.00049	0.00045	0.00053[2]		0.00075
NSD low	0.00051	0.00054	0.00055	0.00063		0.00070
NSD high	0.00051	0.00050	0.00065	0.00095		0.00070
$LSD_{(0.05)}$	ns	ns	0.00015	0.00021		ns

[1]ns = not significant, [2] lime + SOP high 0.00081 mg/l year 1.

Juice Thallium

In general, there was little difference in juice Tl levels between the control and NSD treatments. Perceived differences in Sauvignon Blanc in year 1 were due to site variability since the high lime + SOP rate was also analysed as a second control and had a level intermediate between the two NSD rates. While there are significant differences in juice Tl levels in Pinot Noir in year 3, this is partly due to analytical laboratory buying new equipment with more sensitivity. Irrespective of this, all Tl levels are extremely low. There is no known standard for juice, however for milk in the United Kingdom, levels should ideally be <0.02 mg/l (Roberts and Longhurst, 2001), to protect children. The wine value may therefore be seen as a conservative standard.

Previous monitoring work has shown soil Tl levels decline with depth (Craighead, 2011b; Roberts and Longhurst, 2001). As grapes root very deeply, in excess of 2 m, then it is understandable why herbage and juice Tl levels remain very low irrespective of NSD use. It is difficult to make comparisons between red and white juice, the Sauvignon Blanc site has had a history of more NSD use, whereas with the Pinot Noir the red skins are in contact with the juice during ferment, and so might be expected to have the higher Tl levels. On this property previous analysis of whole fruit, juice or skins has shown Tl levels at or below detection levels irrespective of block, variety or year.

Conclusions

This work has shown that nodulised stack dust (NSD) is an effective source of lime and K for grapes. Its liming component is slightly more available than lime (Morton pers. comm., 1988), possibly due to the kiln dust fineness and the oxides and hydroxides present. By contrast soil K builds up more slowly, particularly in comparison with SOP alone. This is possibly due to a combination of the slower release of the K compounds present in NSD, the Ca in the product competing for soil exchange sites, and because of the NSD granule size and its dissolution rate. Differences between NSD and lime + SOP even out with time.

Although NSD contains Tl, efforts over the past decade have significantly lowered the levels. The influence of NSD on soil, plant and juice Tl levels is measurable and generally rate related. Soil Tl levels have lifted over time, but it would still be many years before these became an issue. More important is herbage (leaf petiole) levels remain very low, and are more influenced by the timing of sampling, hence the low uptake has led to limited transfer to the juice. Therefore as a short to medium term proposition, NSD provides a safe potassium source, its frequency of use to be dictated by soil pH requirements.

The main benefit of NSD is its cost effectiveness. Depending on the transport and spreading costs involved, NSD is 25-50% of the cost of applying SOP, the cost difference depending on whether the liming effect is also required.

The sites in this work were shown to be responsive to K. Soil levels on the best treatments would still be classified as low for grapes, due to the high levels of Mg and there is a need for rates above crop removal and leaf/pruning loss to lift soil K levels.

The rather subjective scoring of leaf greenness as a reflection of K plant uptake, proved to give a reasonable assessment of K sufficiency, in accordance with previous knowledge of the effects of SOP on grapes. It was able to separate the control values from K treatments from year 2. Greenness was however less effective in differentiating between K treatments.

There was no observable difference among treatments with regard to bunch leaf petiole K concentrations, despite bringing sampling forward each year, and foliage correlations with soil K tests were poor. This highlights the pitfall of leaf sampling without the support of other diagnostic measures and observations such as leaf size and canopy growth. In year 3, while leaf analysis was able to differentiate between K rates, the results suggest that differences may need to be large for leaf analysis to be effective.

Although there was a trend for liming products to increase soil pH, the flow on effect to higher juice pH and lower TA was small. Even higher rates of K have not consistently altered juice pH and TA, especially in Pinot Noir, and any K treatment has done this, despite producing darker (greener) vegetation and larger bunches. This is contrary to the practice and understanding of some winegrowers who routinely starve vines in pursuit of the production of quality wine. This work suggests a more measured approach is required, where poorly performing vines and K responsive sites are likely to need K to improve yield and perhaps quality. However, excessive K on soils with good reserves could cause excessive vegetation, and dilute and delay sugar formation. High K reserve soils may only require 0-40 kg K/ha while 40-80 kg K/ha is necessary for medium reserve soils. In New Zealand few grape vines are grown on low K reserve soils. With small profit margins, it makes economic sense for growers to produce more juice of a similar quality for the small cost of K fertiliser (likely to be 1-5% of a grower's costs). This will go some way to improving sustainability and reducing the carbon footprint in the wine industry.

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